Fluoride Reuse in Aluminum Trifluoride Manufacture: Sustainability Criteria

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INTRODUCTION

Sustainable Development has been introduced in the chemical engineering objectives related to processes, plants and systems. It is a model of progress that links economic development, protection of the environment and social responsibility [1]. This concept aims to harmonize the economical, social and environmental dimensions of the development strategies and it is now a key feature of the policy making in the European Union (EU). Sustainable Development is related to: balanced and equitable economic development; high levels of employment, social cohesion and inclusiveness; and a high level of environmental protection and responsible use of natural resources.

The objective of the environmental policy in the EU consists of preventing, reducing and as far as possible eliminating pollution by giving priority to intervention at source and ensuring the sustainable management of natural resources, in compliance with the principles of pollution prevention [2]. The goal is an Integrated Prevention and Pollution Control Policy able to reduce the emissions in order to promote a Sustainable Development.

The design approach of pollution prevention consists in a hierarchy of different steps [3]: 1) minimize generation of pollution; 2) minimize materials and energy consumption. This hierarchy holds for preventing pollution during design or in fact any other engineering action. Every action should be focused on minimization of the generation of waste or the introduction of waste.

Until recently, environmental solutions to processing facilities occurred mainly in the form of end-of-pipe pollution control strategies. These solutions focus primarily on chemical, biological and physical treatment of waste streams leaving the plant, reducing the toxicity and volume of pollutants in industrial discharges. Although these pollution control strategies have often resulted in significantly reducing environmental consequences of processing facilities, they lacked cost-effectiveness and sustainability.

In this work it has been analyzed the AlF_3 production in a Spanish plant as basic inorganic product in terms of sustainability. The recovery of fluoride from industrial wastewaters as a product to be reused is presented as priority objective of the fluorine industry in order to contribute to the sustainable development.

ALUMINUM FLUORIDE MANUFACTURE

Aluminum fluoride (AlF_3) is primarily used as a fluxing agent for the electrolysis of aluminum, but also in the glass industry and in the enamel industry for the production of white enamels.

The dry fluorspar process is the worldwide dominating process, counting for approximately 65% of total AlF_3 production. The main raw materials are fluorspar (CaF_2), aluminum hydroxide ($Al(OH)_3$) and sulphuric acid (H_2SO_4). The two main steps of the process are: (1) the generation of gaseous HF from fluorspar and sulphuric acid and, (2) the production of AlF_3 from gaseous HF and $Al(OH)_3$ (activated to Al_2O_3).

Generation of gaseous HF

Dried fluorspar and sulphuric acid are preheated to 120-150ºC and fed into a rotary kiln reactor, the pre-conversion is usually 30-50%. The reaction is completed in a directly or indirectly heated kiln where the temperature of the reactants is raised to 200-300ºC at the outlet end of the kiln. The overall reaction can be described by the following equation:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF \qquad (1)$$

Gypsum (synthetic anhydrite) is removed from the rotary kiln outlet end as a by-product and either transported to a landfill as a waste or reused as construction material. The anhydrite is then cooled down and traces of sulphuric acid are neutralized with lime before the product is ground to the required size for commercial purposes. Synthetic anhydrite from AlF_3 plants is used mainly for the construction of self-leveling floors, as an additive to cement production and in the fertilizer industry.

The effluent gas from the rotary kiln after separation/concentration contains 40-100% HF and it is passed through scrubbers to remove dust, elemental sulphur and the impurities before it is used in the AlF_3 manufacture step.

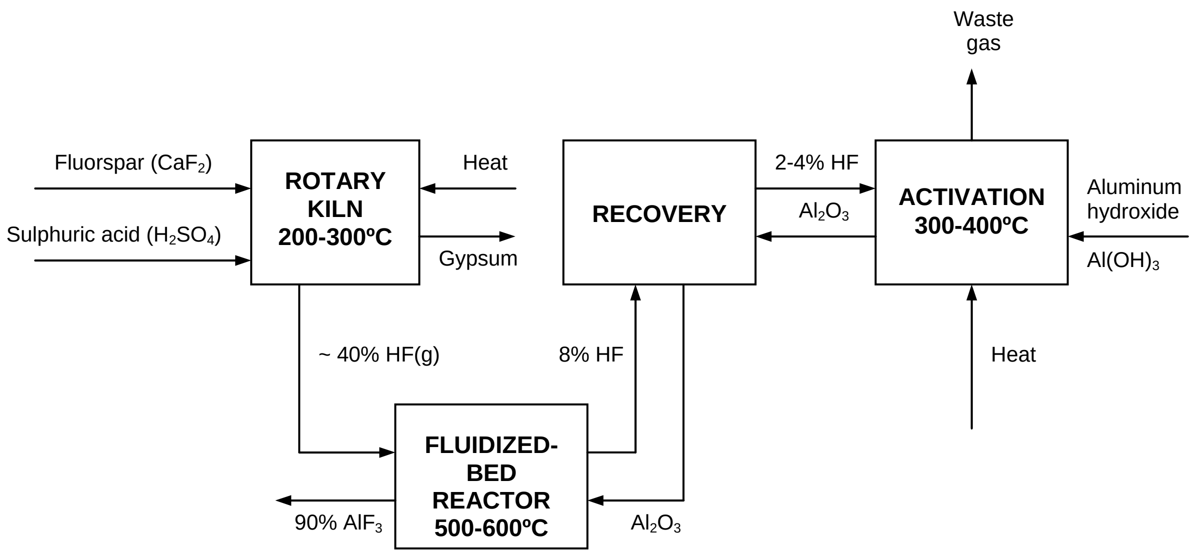

Figure 1. Flow-sheet of aluminum fluoride production by the dry fluorspar process [4].

AlF_3 production

$Al(OH)_3$ is transformed to Al_2O_3 by heating it up to approximately 400ºC, and Al_2O_3 is the fed into a fluidized bed reactor where the reaction with gaseous HF takes place according to the following overall equation:

$$Al_2O_3 + 6\ HF \rightarrow 2\ AlF_3 + 3\ H_2O \qquad (2)$$

This reaction takes place in a single or multi- fluidized bed reactor. Depending on the HF recovery system, a yield of 94-98% based on HF entering the aluminum fluoride reactor is achieved.

The flow sheet of aluminum fluoride production by the dry fluorspar process is given in Figure 1.

Abatement techniques

Gaseous effluent from the production of AlF_3 are cleaned by passing the gas through one or several wet scrubbers for the removal of HF, sulphur compounds and dust before being emitted to the atmosphere. The emissions of HF are reduced to >99% in this type of treatment system and wastewater containing fluoride is produced in the gas cleaning operations.

Materials and Energy Consumption

Typical materials and energy consumption in the dry fluorspar process are summarized in Table 1.

Table 1. Consumption of raw materials and energy carriers [4].

Raw material / energy carrier	Typical consumption level (per tonne AlF_3 produced)
CaF_2	1.54 t/t
H_2SO_4	1.85 t/t
$Al(OH)_3$	1.03 t/t
$Ca(OH)_2$	0.03 t/t
Fuel	4.5 GJ/t
Electricity	0.165 MWh/t
Steam	0.2 t/t

A range of specific emissions to air from an AlF_3 plant using the dry fluorspar process is given in Table 2.

Table 2. Emissions to air-dry fluorspar AlF_3 production process [4].

Component	Specific discharges (per tonne AlF_3 produced)
SO_2	0.07 kg/t
NO_x	0.39 kg/t
CO_2	0.41 t/t
Fluoride	0.01 kg/t
Dust	0.05 kg/t
Hg	0.08 g/t

In turn, a range of specific emissions to water from AlF_3 plant using the dry fluorspar process is shown in Table 3.

Table 3. Discharges to water-dry fluorspar AlF_3 production process [4].

Component	Specific discharges (per tonne AlF_3 produced)
SO_2	71.7 kg/t
Fluoride	5.1 kg/t
Hg	0.04 g/t
Pb	0.16 kg/t
Sulphuric acid	15.0 kg/t

And Table 4 shows the residual solid materials involved in the process.

Table 4. Solid wastes-dry fluorspar AlF_3 production process.

Component	Solid Wastes (per tonne AlF_3 produced)
Gypsum	2.4 t/t
CaF_2 (sludge)	115 kg/t

FLUORIDE REMOVAL FROM INDUSTRIAL WASTEWATERS

Fluoride containing wastewater is an industrial effluent requiring neutralization due to the acidity and fluoride concentration control. Fluoride is a regulated pollutant and therefore it is necessary some treatment to reduce its concentration below the required limits.

Several methods to remove fluoride from industrial wastewater have been described and applied:

Chemical precipitation

Precipitation is the most common treatment technology to remove fluoride from industrial wastewaters. Chemical precipitation is a physico-chemical process, comprising the addition of lime or hydrated lime to wastewater, causing precipitation of an insoluble product that is settled out by sedimentation. Anionic polymers may be used to assist solid-liquid separation.

This fluoride removal generates huge amounts of a water rich sludge, which has to be disposed off with increasing costs. The high water content (50-60%) and the low quality of the solid material (40-60% of CaF_2) prevent technical and economically the recovery of precipitated fluoride [5].

Figure 2 shows the material flow of the AlF_3 production, including the removal of fluoride from wastewater by chemical precipitation.

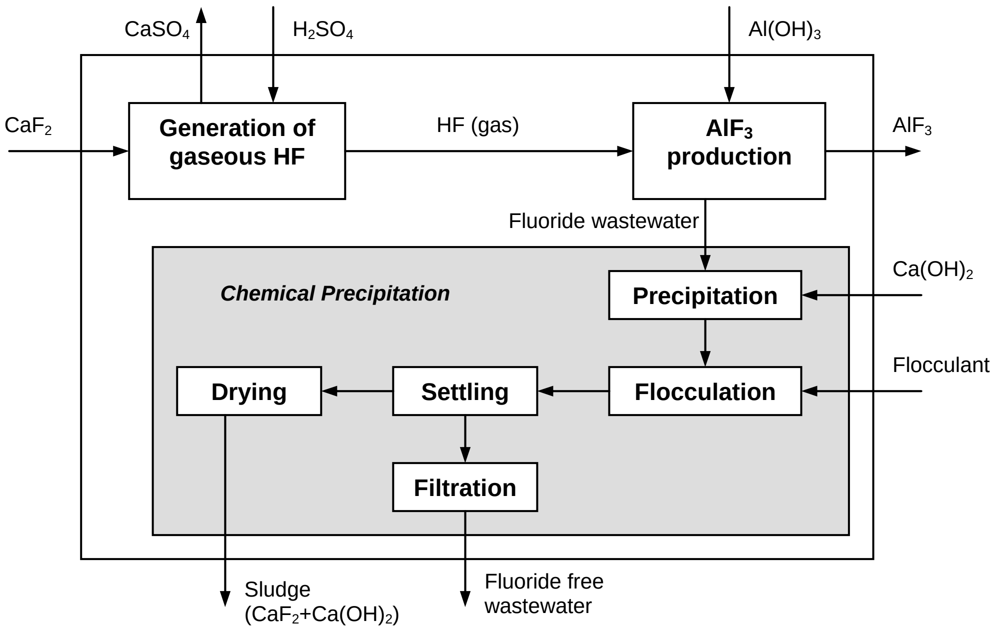

Figure 2. Flow-sheet in AlF_3 production including removal of fluoride wastewater by chemical precipitation.

Crystallization in a pellet reactor

Process description

The fluidized bed reactor (FBR) technique process has been used in various water and wastewater treatment plants. A pellet reactor, which is a reactive fluidized-bed growth-type crystallizer, has been developed for water softening of drinking water [6,7], phosphate [8] and fluoride removal [9,10], and heavy metal recovery from wastewaters [11-14].

The chemistry of the process is similar to the conventional precipitation. By dosing calcium hydroxide to the wastewater, the solubility of CaF_2 is exceeded and fluoride is converted from the aqueous solution to solid crystals according to the following reactions:

$$H^+ + F^- \rightarrow HF \qquad (3)$$

$$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2 \qquad (4)$$

$$Ca^{2+} + 2F^- \rightarrow CaF_2(s) \qquad (5)$$

The main difference with the common precipitation lies on the fluidized bed reactor. The process is based on the crystallization of calcium fluoride upon seed material (silica sand or granular calcite) instead of mass precipitation in the liquid phase.

During the operation, the grains increase in diameter in the fluidized bed reactor. A bed of large grains has small reactive surface and therefore the fluoride-covered grains are removed from the bottom of the bed and replaced by fresh seed grains. The growth of seed material-calcium fluoride takes place by molecular growth and aggregation between the seed grains and the formed calcium fluoride in the liquid phase (nucleated precipitation). Figure 3 shows the proposed mechanism of calcium fluoride pellets formation.

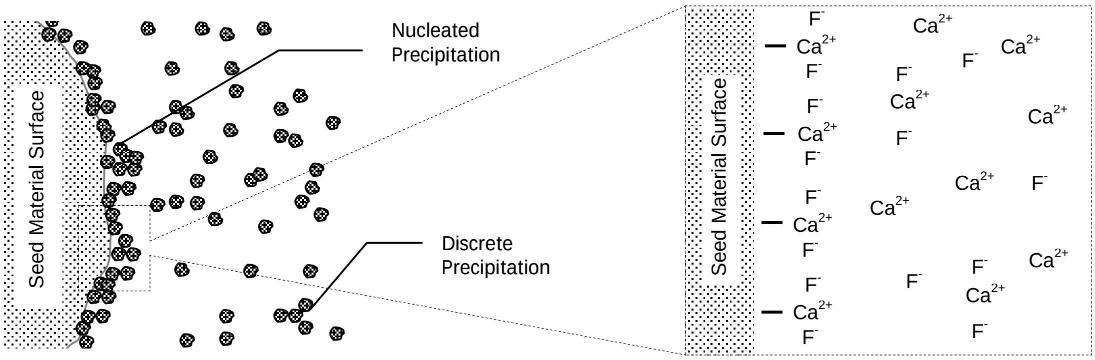

Figure 3. Precipitation mechanism upon seed material in a fluidized bed reactor.

The molecular growth and aggregation with the sand grains takes place together with discrete precipitation in the liquid phase (primary and secondary nucleation) and mineral layer abrasion. Nucleation in the liquid phase and abrasion of the grains in the fluidized bed leads to small particles (referred to as fines), which leave the reactor at the top and form, together with the remaining fluoride in solution, the fraction of the fluoride that is not possible to recover in the reactor. The set-up of the reactor and streams is described in Figure 4.

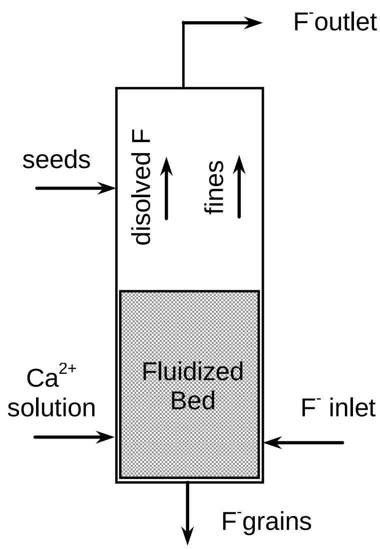

Figure 4. Schematic representation of a fluidized bed reactor for fluoride removal.

Low supersaturation implies nucleated precipitation. On the contrary, when the system is operated at higher supersaturation primary nucleation occurs leading to the formation of many nuclei (discrete precipitation), which are not possible to be retained in the reactor, not even by aggregation with silica sand. In these conditions, the efficiency of the process is lower increasing the turbidity of the effluent. Therefore, it is very important to control the supersaturation in the fluidized bed reactor by means of a fluoride inlet concentration lower than 150 $mg{\cdot}L^{-1}$ [5].

Appropriate supersaturation conditions at the inlet of the reactor are not possible when the fluoride wastewater presents high fluoride concentration. In this case, it is necessary to dilute the fluoride wastewater to prevent primary nucleation. However, secondary nucleation seems to be the origin of the new fines formation in the reactor decreasing the nucleated precipitation. The use of a sand filter bed improves the efficiency of the process when recycling of the effluent is necessary. The efficiencies of the continuous process can be reached using a filter bed to avoid secondary nucleation.

Synthetic calcium fluoride

Figure 2 shows the obtained calcium fluoride pellets from silica sand (a) and granular calcium fluoride (b) as seed material. Pellets with calcium fluoride content higher than 97%, and particle size about 900 μm have been obtained. Table 5 shows the main properties of the obtained pellets of calcium fluoride in comparison with the precipitation sludge.

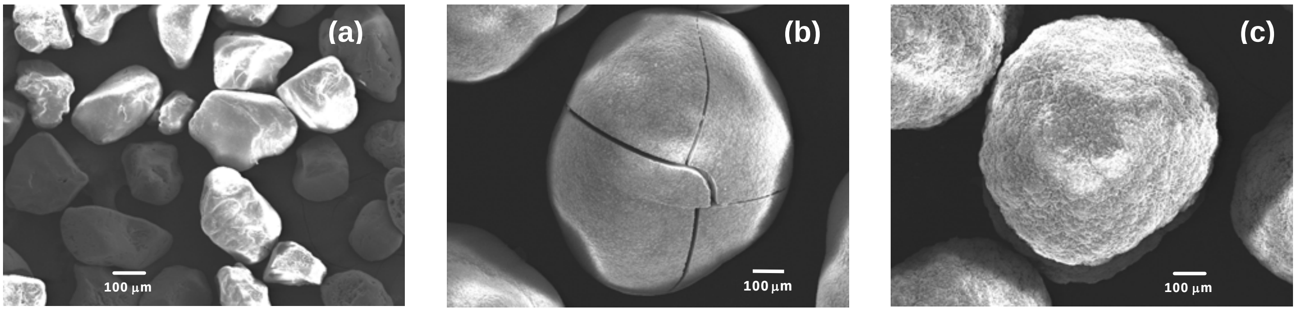

Figure 2. SEM of seed material (silica sand) (a), and CaF_2 from SiO_2 seed material (b) and $CaCO_3$ seed material (c).

Table 5. Calcium fluoride characterization from crystallization and classical precipitation.

Parameter	Crystallization	Precipitation
Morphology	Pellets (0.8-1.0 mm)	Sludge (1-10 μm)
Water Content	<5 %	50-60 %
CaF_2 content	>97 %	40-60%
SiO_2	<1,5%	-
$CaCO_3$	<1%	20-30%

Due to the composition and the low water content, reuse of the recovered calcium fluoride is possible as synthetic fluorite, which can be reused in the first step of the process avoiding the sludge formation and leading to the reduction of solid waste.

Recovery of synthetic calcium fluoride

The recovery of fluoride by crystallization is an example of process intensification. The idea behind process intensification is the optimal integration of energy, materials, and processing tasks with the goal of minimizing amounts of energy and materials needed and size of equipment required to produce a given quantity of product per unit time.

In this sense, the main advantages of the crystallization in a fluidized bed reactor to recovery of fluoride from industrial wastewater are: compact and flexible unit, thus enabling modular set-up and tailor-made materials selection; no sludge production; water-free pellets with high purity which enables recycling or further usage of the fluoride content in other sectors; raw material recovery/recycling; nearly waste-free process. From Table 4 it is possible to deduce that the crystallization in a pellet reactor allows to recover 115 kg of synthetic calcium fluoride per tonne of aluminum trifluoride produced. In these conditions, it is possible to save near 8% of fluorspar as raw material allowing the reduction of sludge.

Figure 3 shows the material flow in AlF_3 production including removal of fluoride wastewater by crystallization in a fluidized bed reactor.

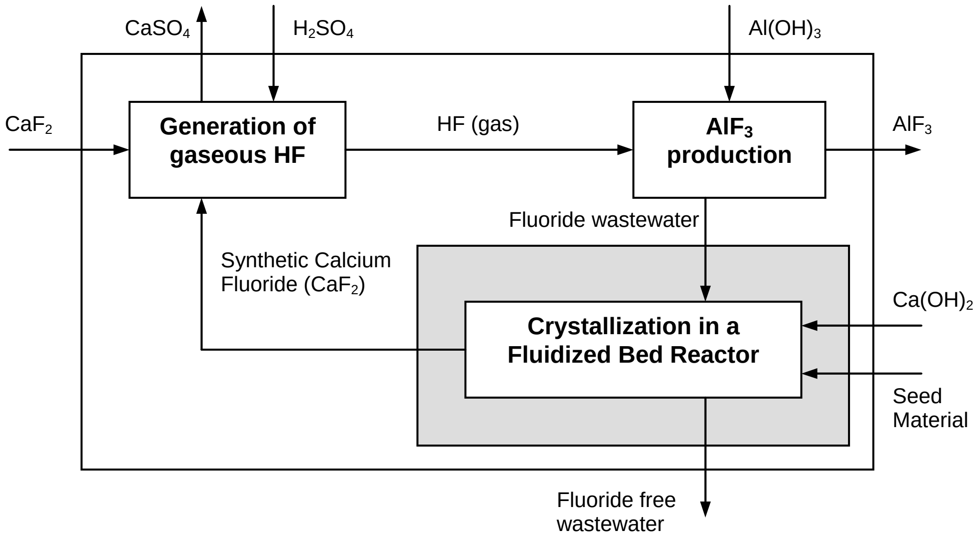

Figure 3. Material flow in AlF_3 production including removal of fluoride wastewater by crystallization in a fluidized bed reactor.

Table 6. Estimate costs and benefits evaluation [5].

Type of costs	Costs[a] [USD/kg]	Remarks
Capital costs		depending on capacity
Operating costs		
Depreciation	3-25	depending on capacity
Chemicals	0.50-2.50	depending on concentration
Energy	0.25	
Staff		1 hour per day
Maintenance		3-5% of investment
Benefits		
Reuse	0-14.50	
Reduction of chemical waste	2-8	depending on concentration in sludge
Saving on investment for precipitation plant	3-12	in the case of final treatment
Reduction of discharge fee	30-40	in the case of final treatment

[a] per kg recovered anion

The operating costs in the crystallization process are similar to the conventional precipitation. Nevertheless the derived benefits are important (reuse, reduction of chemical waste and reduction of discharge fee). Table 6 shows an estimate costs and benefits evaluation.

CONCLUSIONS

As a conclusion it has been shown that the crystallization process to obtain synthetic fluorite can be considered a sustainable technology due to the intensification in the materials benefit and its application in the fluorine industry may contribute to the reduction of waste materials and the optimization of raw materials consumption.

The economical benefits have been also evaluated and they allow to justify the new crystallization process investment.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the Ministry of Science and Technology of Spain trough the project No. PPQ2003-00546.

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